U.S. DEPARTMENT OF ENERGY | Nuclear Energy

Behavior of Zirconium Oxide and Zirconium Metal in a LiCl-Li_2O-Based Electrolytic Reduction System

S. D. Herrmann, L. A. Wurth, N. J. Gese

August 27, 2012

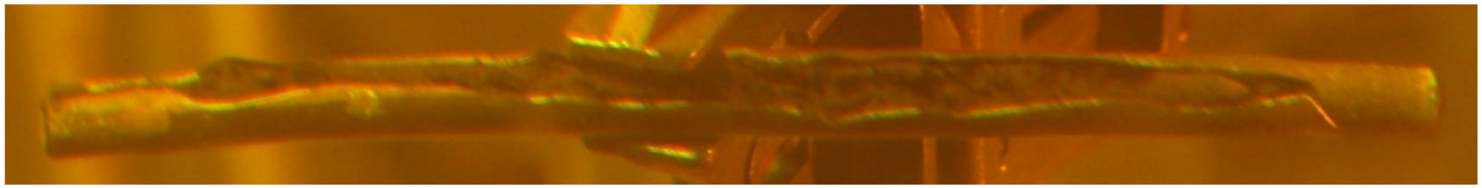
2012 International Pyroprocessing Research Conference

The Abbey Resort
Fontana, Wisconsin

Introduction

Background

- An electrometallurgical treatment process has been operating since 1996 to treat 25 MTHM of sodium-bonded uranium metal blanket and uranium metal alloy driver fuel from Experimental Breeder Reactor – II (EBR-II) at Idaho National Laboratory's Fuel Conditioning Facility.
- In the course of retrieving EBR-II spent driver fuel for treatment, a significant quantity of degraded U-10Zr spent fuels, i.e., breached fuel exposed to air, has accumulated since 1996.
- As oxidized material, it would require head-end treatment prior to electrorefining.
- Electrolytic reduction is a candidate head-end treatment process that could facilitate subsequent electrorefining.
- However, degraded U-10Zr would introduce significant quantities of partially to fully oxidized zirconium into a $LiCl-Li_2O$ electrolytic reduction system at 650 °C, in which the behavior of zirconium oxide and zirconium metal is not well defined.



Degraded EBR-II fuel element

Test Objectives and Approach

Objectives

- Define behavior of zirconium oxide and zirconium metal in LiCl-Li_2O at 650 ° C.
- Determine whether or not zirconium oxide can be reduced to metal in a LiCl-Li_2O electrolytic reduction system.

Approach

- Contact zirconium oxide and zirconium metal separately in LiCl-Li_2O at 650 ° C and assess behavior (without electric potential).
- Perform bench-scale electrolytic reduction of MnO particulate (surrogate for UO_2) and MnO-ZrO_2 particulate blend and assess behavior (with electric potential).

No.	Test Conditions
1	ZrO_2 particulate addition to LiCl-Li_2O at 650 °C
2	Zr metal wire immersion in LiCl-Li_2O at 650 °C
3	Zr metal particulate addition to LiCl-Li_2O at 650 °C
4	Electrolytic reduction of MnO particulate in LiCl-Li_2O at 650 °C
5	Electrolytic reduction of MnO-ZrO_2 particulate in LiCl-Li_2O at 650 °C

Technical Basis

Thermodynamic Stabilities*

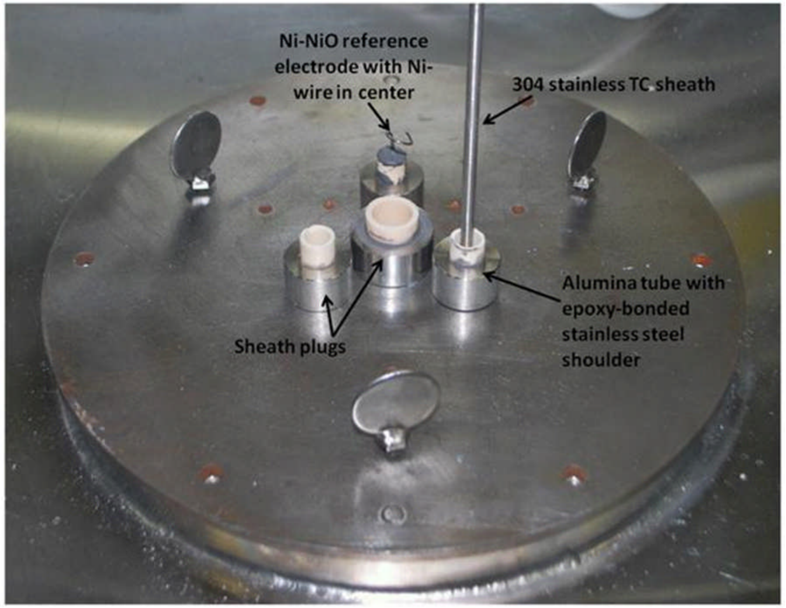
Compound	ΔG_f at 650 °C (kJ / mol O)	ΔG_f at 650 °C (kJ / mol Cl)	E° (V)
MnO	-317.21		1.64
ZrO_2	-461.95		2.39
UO_2	-462.65		2.40
Li_2O	-475.73		2.47
Li_2ZrO_3	-488.49		2.53
$LiCl$		-333.71	3.46

Possible Reaction Mechanisms*

- $ZrO_2 + Li_2O \rightarrow Li_2ZrO_3$ ($\Delta G_{f,\ 650C} = -66$ kJ)
- $Zr + 3\ Li_2O \rightarrow Li_2ZrO_3 + 4\ Li$ ($\Delta G_{f,\ 650C} = -38$ kJ)

**Ref: HSC Chemistry 7.1*

Equipment and Materials



- **Solid – Liquid Contacting**
  - Jeweler furnace (650 ° C)
  - Argon atmosphere glovebox
  - 2.5 cm dia. x 10 cm MgO crucible (~50 ml)
  - 36 – 50 g LiCl (AAPL, 99.99+%, anhydrous)
  - 3.5 wt% Li_2O (Alfa Aesar, 99.5%)
- **Electrolytic Reduction**
  - Molten Salt Furnace – II (650 ° C)
  - Same argon atmosphere glovebox
  - 10 cm dia. x 11 cm MgO crucible (~500 ml)
  - 750 g LiCl (AAPL, 99.99+%, anhydrous)
  - 1 wt% Li_2O (Alfa Aesar, 99.5%)
  - Ni/NiO reference electrode

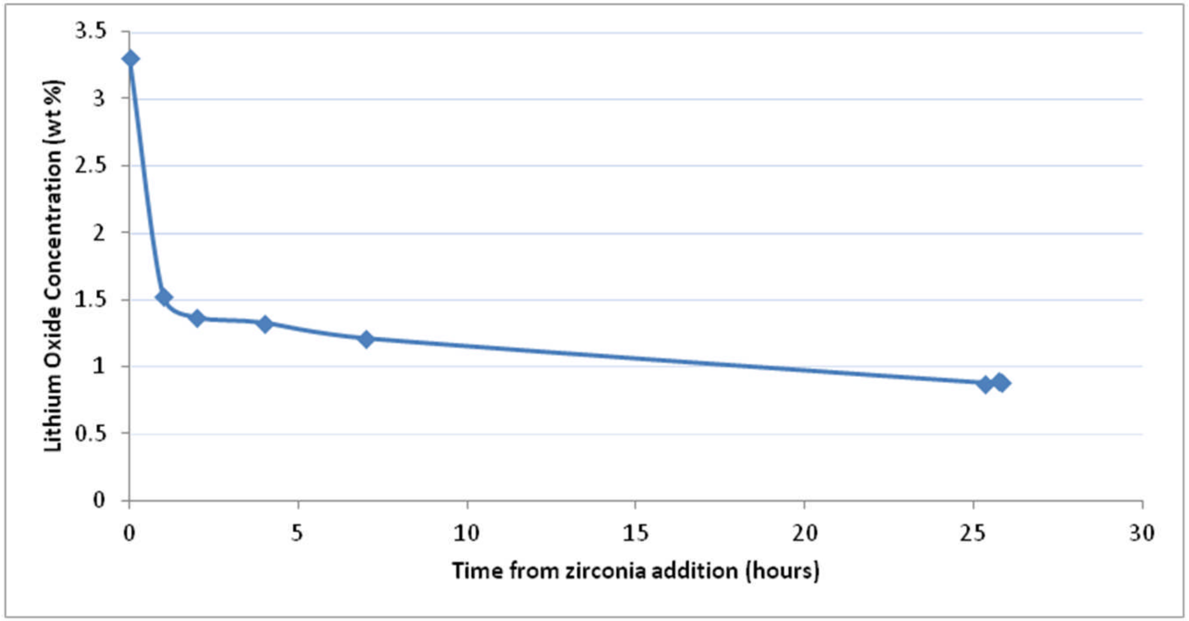
ZrO_2 in LiCl-Li_2O Test (no. 1)

Procedure

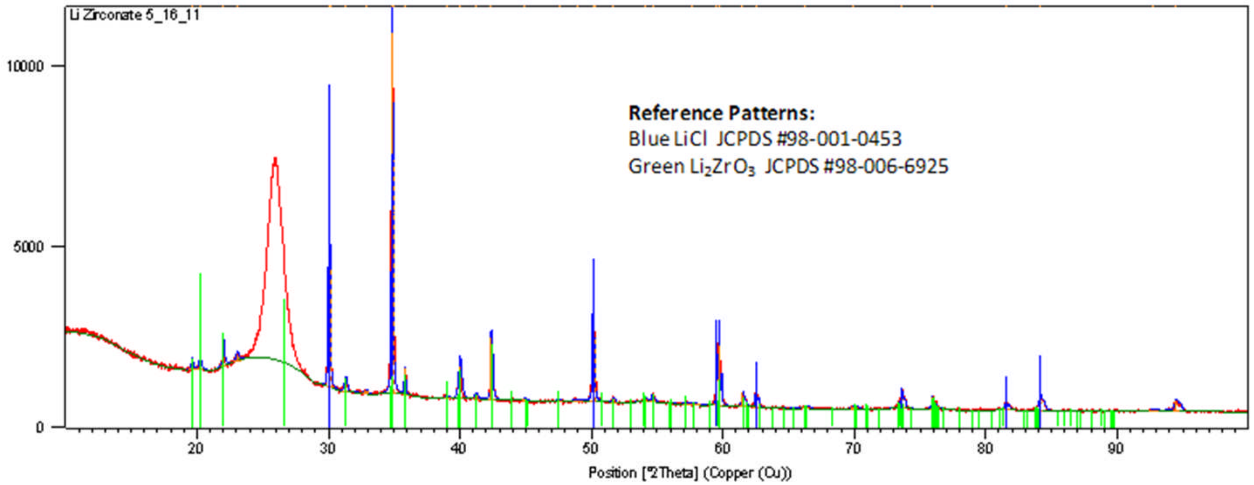
- Prepared LiCl – 3.5 wt% Li_2O (35.76 g LiCl, 1.29 g Li_2O)
- Added 4.58 g ZrO_2 particulate (Alfa Aesar, 99%)
- Took time-at-temperature salt samples over 26-hr period
- Analyzed salt samples for Li_2O concentration.
- Performed XRD on post-test solid phase particulate.

Pre- and post-test crucible loadings

ZrO_2 in LiCl-Li_2O Test Results (no. 1)



Li_2O concentrations in time-at-temperature salt samples via water dissolution and titration

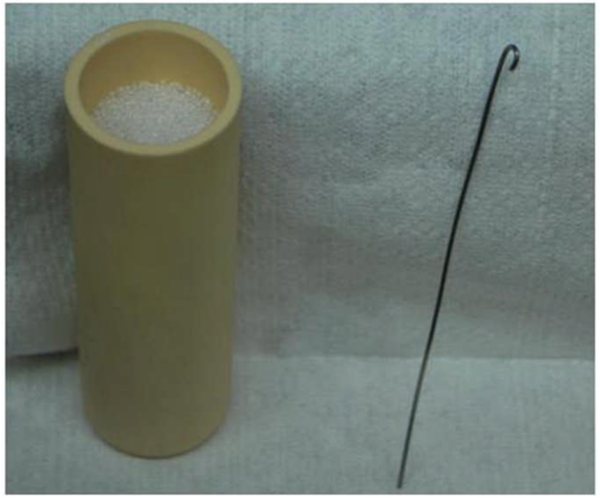


XRD analysis of solid particulate phase

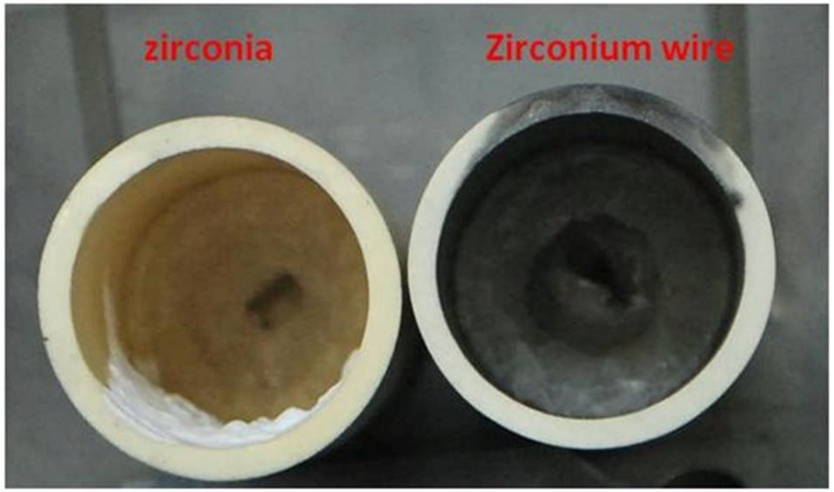
Zr Wire in LiCl-Li_2O Test (no. 2)

Procedure

- Prepared LiCl – 3.5 wt% Li_2O (49.43 g LiCl, 1.79 g Li_2O)
- Immersed 1 mm dia. Zr wire to 7 cm depth.
- Held wire at temperature for 72 hours.
- Performed SEM on post-test wire.

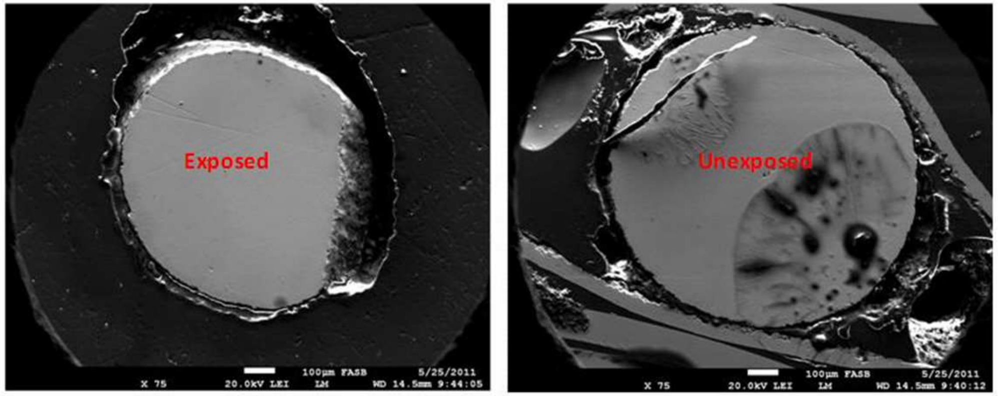


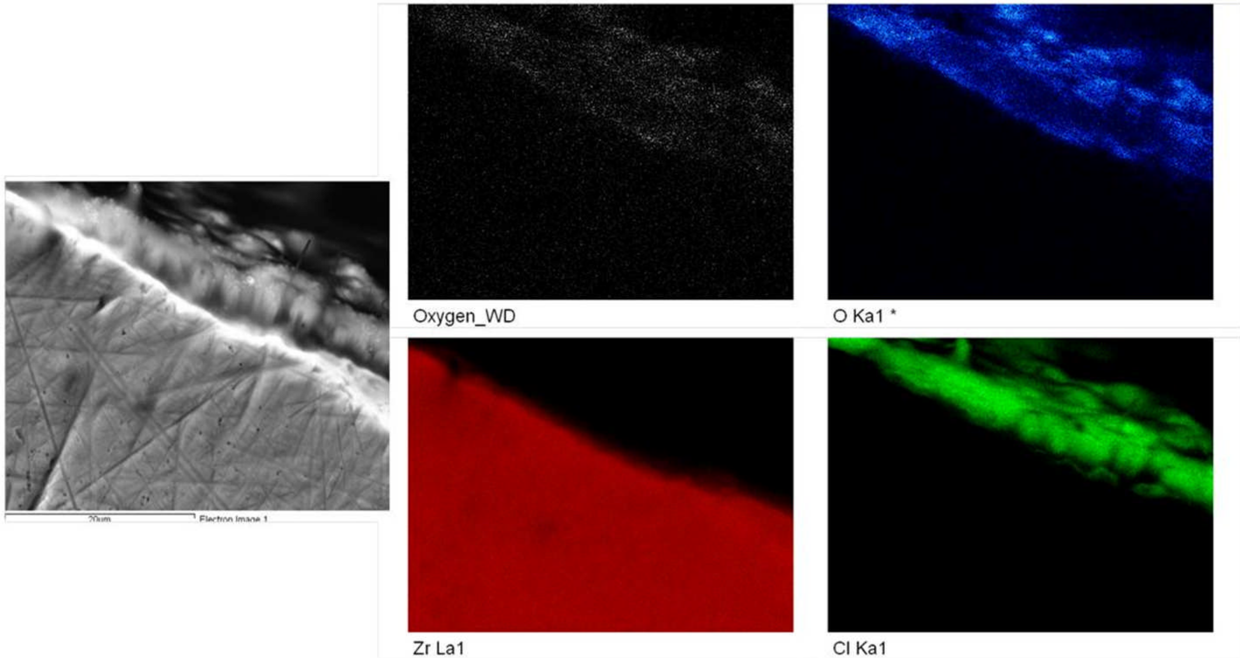
Pre-test materials



Comparison of post-test crucibles from test 1 (left) and test 2 (right)

Zr Wire in LiCl-Li_2O Test Results (no. 2)



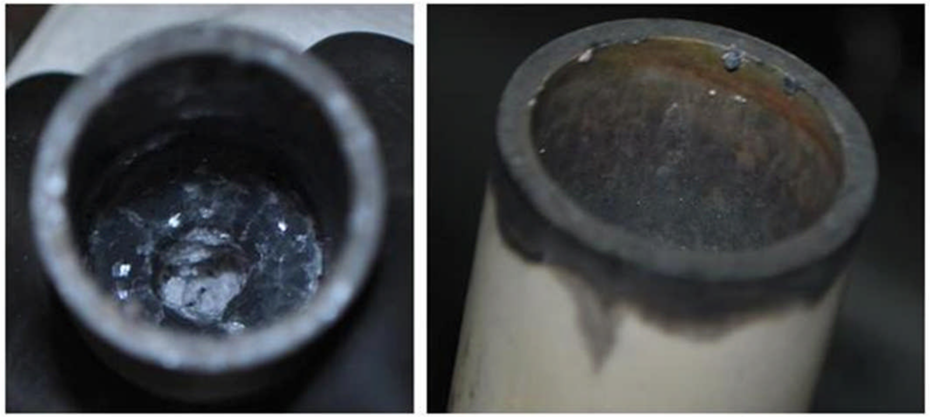


- Visual and SEM images of post-test Zr wire
- Observed 28% reduction in cross-sectional area of wire.

Zr Metal Particulate in LiCl-Li_2O (no. 3)

Procedure

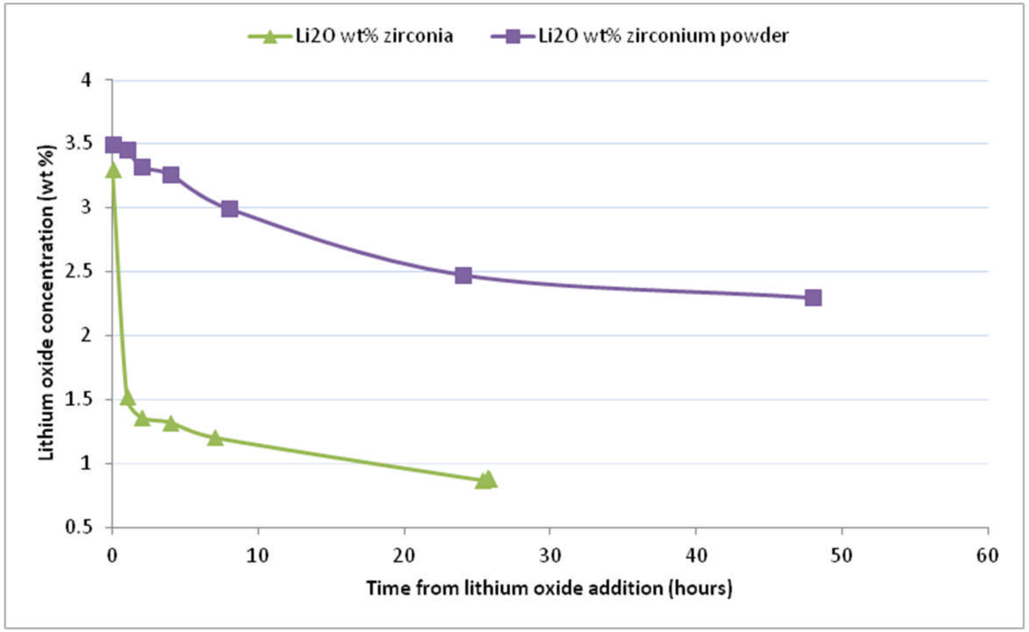
- Heated 36.63 g of LiCl and 1.15 g of Zr metal particulate (CERAC, 99.8%, -140, +325) to 650 °C and held for 24 hours
- Observed colorless salt and no color change to MgO crucible after 24 hours
- Added 1.33 g Li_2O to create a LiCl – 3.5 wt% Li_2O solution
- Observed darkening of salt within first hour of Li_2O addition
- Took time-at-temperature salt samples over 48-hr period
- Analyzed salt samples for Li_2O concentration.
- Performed XRD on post-test solid phase particulate.



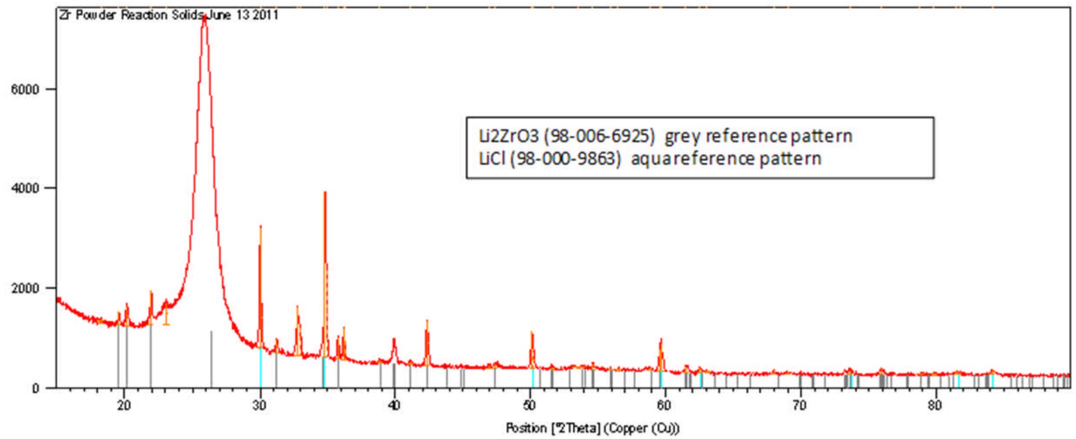
post-test crucible

wire mesh ladle used to remove post-test solid phase particulate sample

Zr Metal Particulate in LiCl-Li_2O Test Results (no. 3)



- Li_2O concentrations in time-at-temperature salt samples via water dissolution and titration
- Plot shows comparison of Li_2O depletion between ZrO_2 and Zr metal particulate additions
- Observed fizzing upon dissolution of salt samples following Zr metal addition, but not ZrO_2



XRD analysis of solid particulate phase

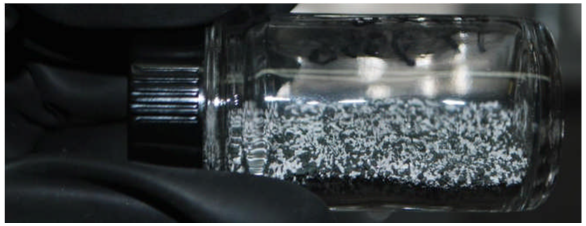
Electrolytic Reduction – Operating Conditions

Operating Conditions in Molten Salt Furnace – II

- Electrolyte: LiCl – 1 wt% Li_2O, 650 ° C, ~ 500 ml
  - *Loaded magnesia crucible with 750 g LiCl*
  - *Loaded Li_2O incrementally to produce 0, 0.5 and 1 wt% Li_2O concentrations in LiCl*
- Cathode: Stainless steel wire mesh basket (1.9 cm dia. x 7.6 cm, 325 mesh)
- Anode: 1 mm dia. Pt wire, spiral wound, 10 cm^2
- Reference Electrode: Ni/NiO in magnesia tube with porous end plug
- Power Supply: Biologic VSP

Procedure

- Performed cyclic voltammetry in molten salt with stainless steel and platinum working electrodes, Mo-wire coil counter electrode, and Ni/NiO reference electrode.
- Performed electrolytic reduction of MnO particulate (27.53 g) followed by blended MnO-ZrO_2 particulate (17.94 g and 9.07 g, respectively) in same salt.

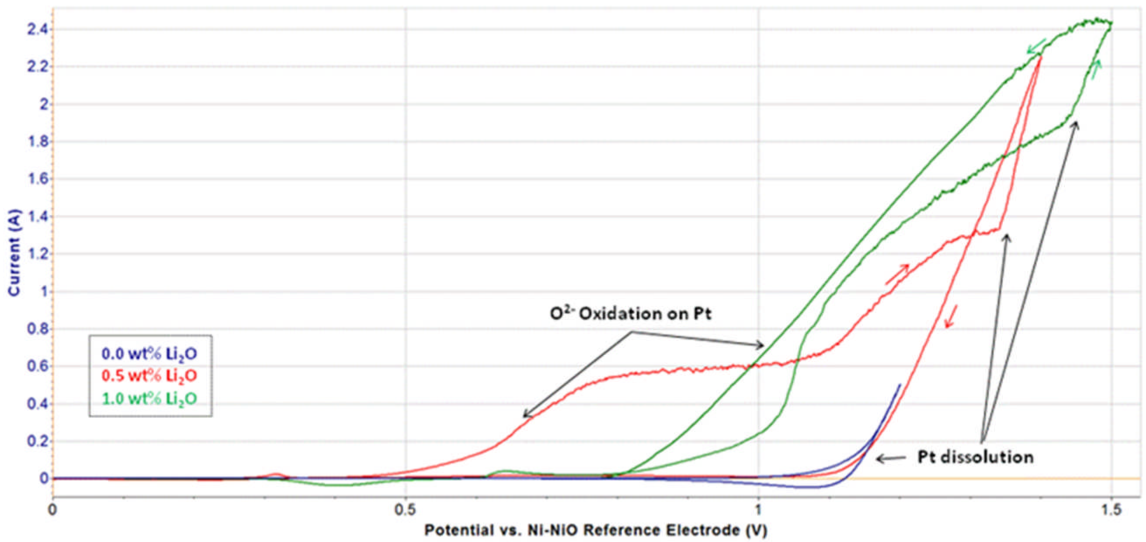


blended MnO (dark) and ZrO_2 (white) particulate

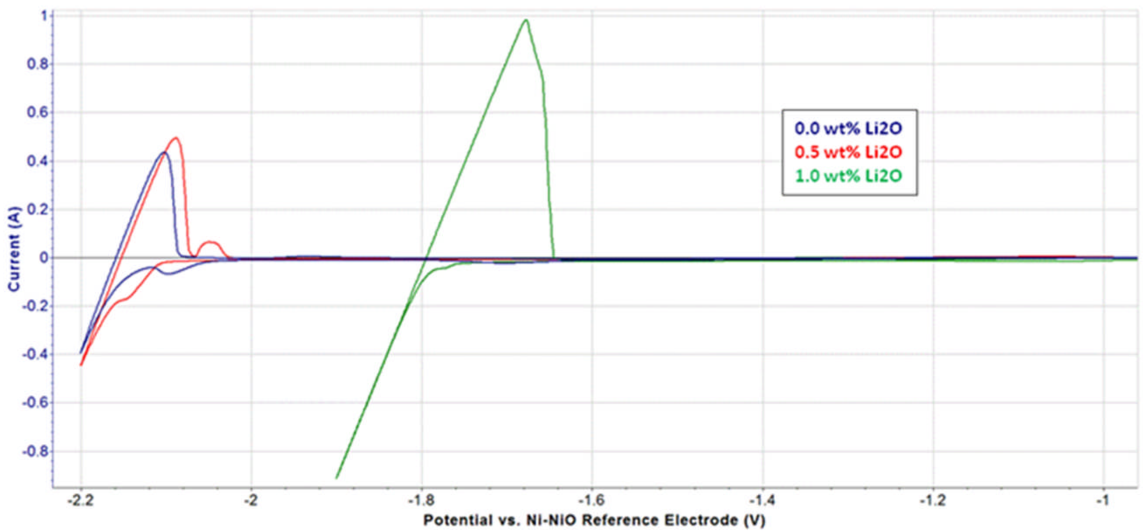
U.S. DEPARTMENT OF ENERGY

Nuclear Energy

Electrolytic Reduction – Cyclic Voltammetry



Pt wire working electrode

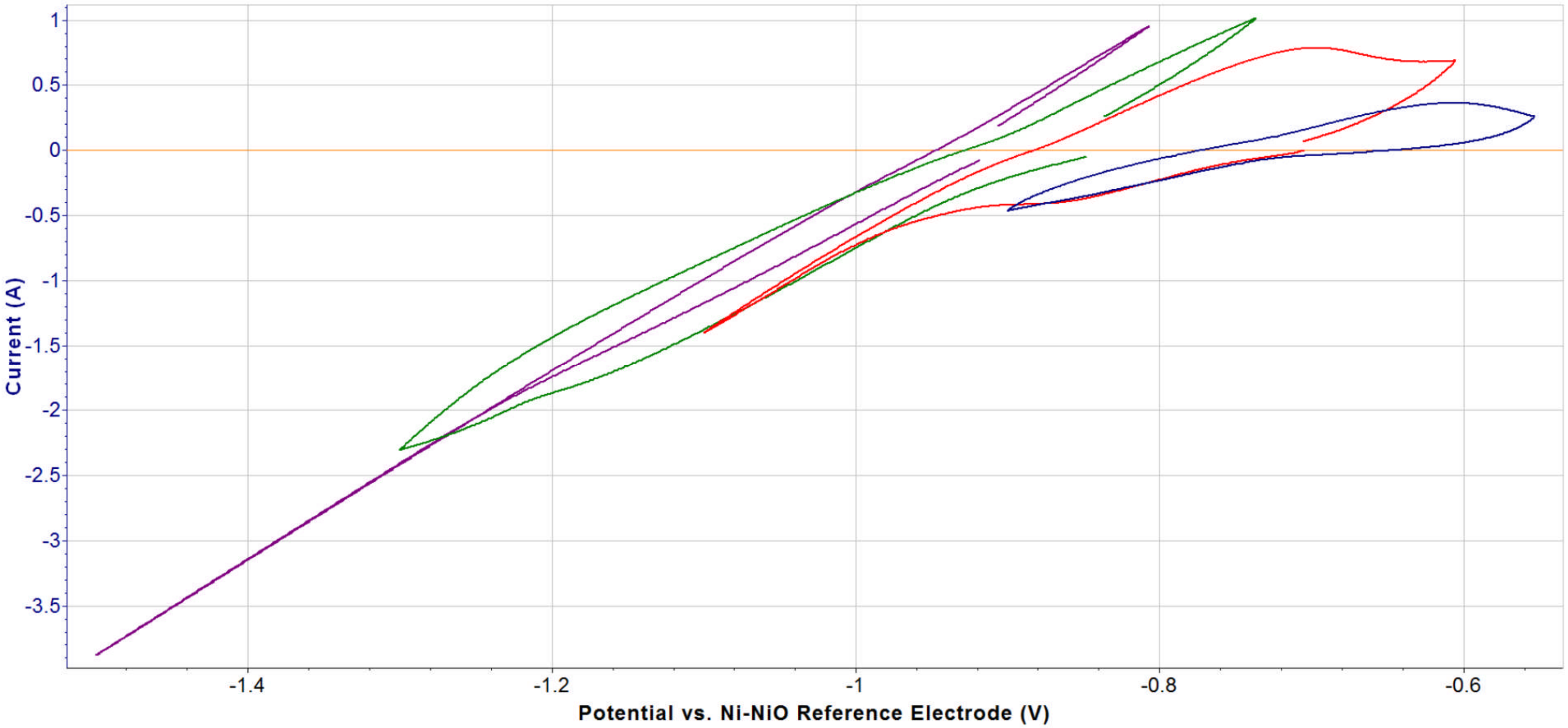


SST wire working electrode

U.S. DEPARTMENT OF ENERGY

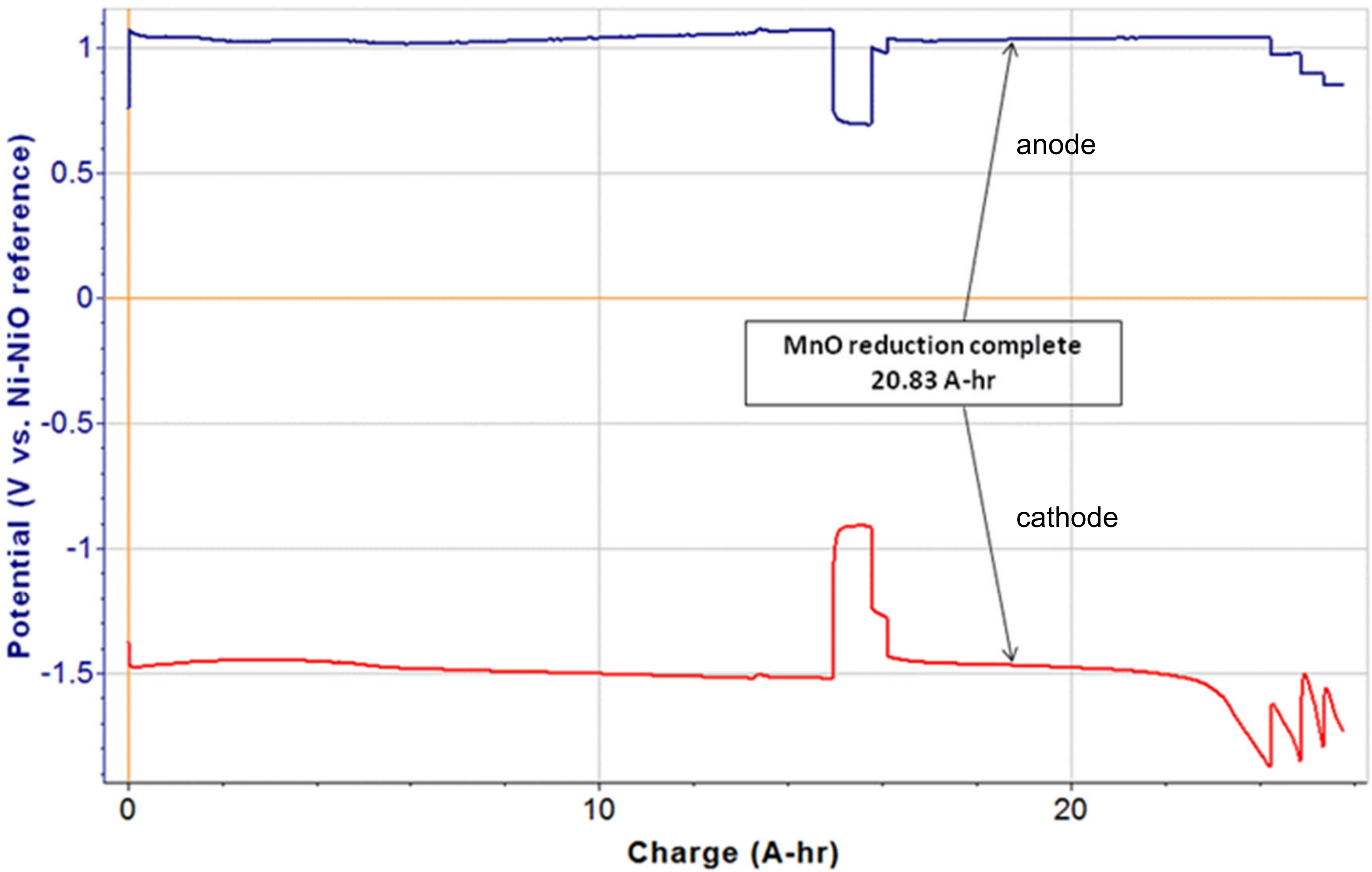
Nuclear Energy

Electrolytic Reduction – Cyclic Voltammetry (cont.)

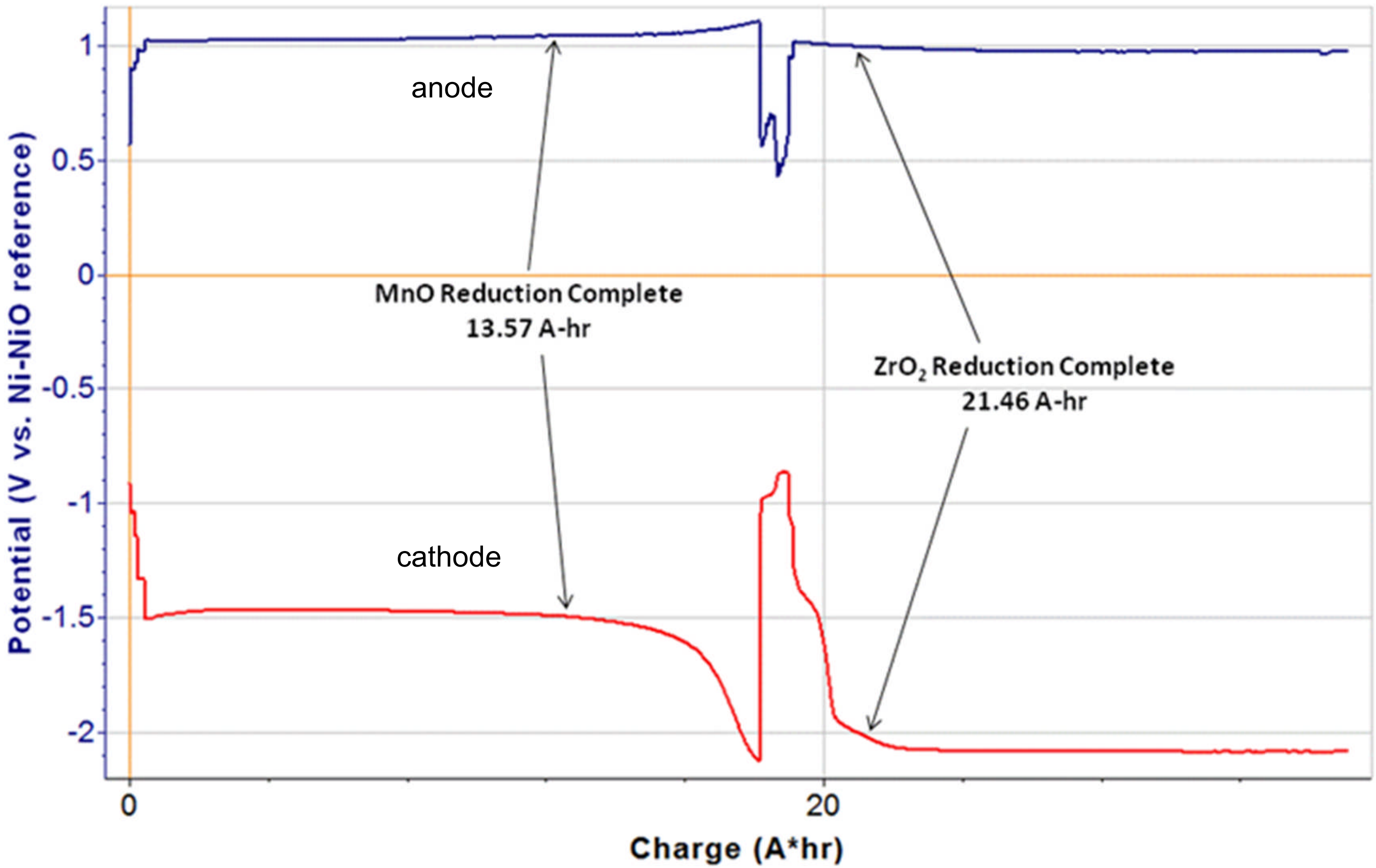


MnO loaded SST wire mesh basket as working electrode

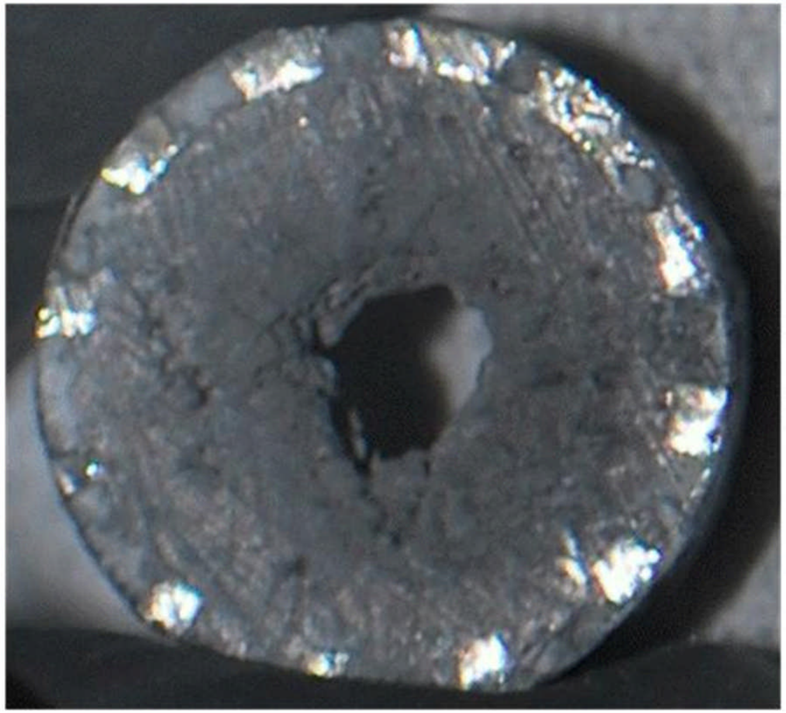
Electrolytic Reduction of MnO – Response Plot (Test 4)



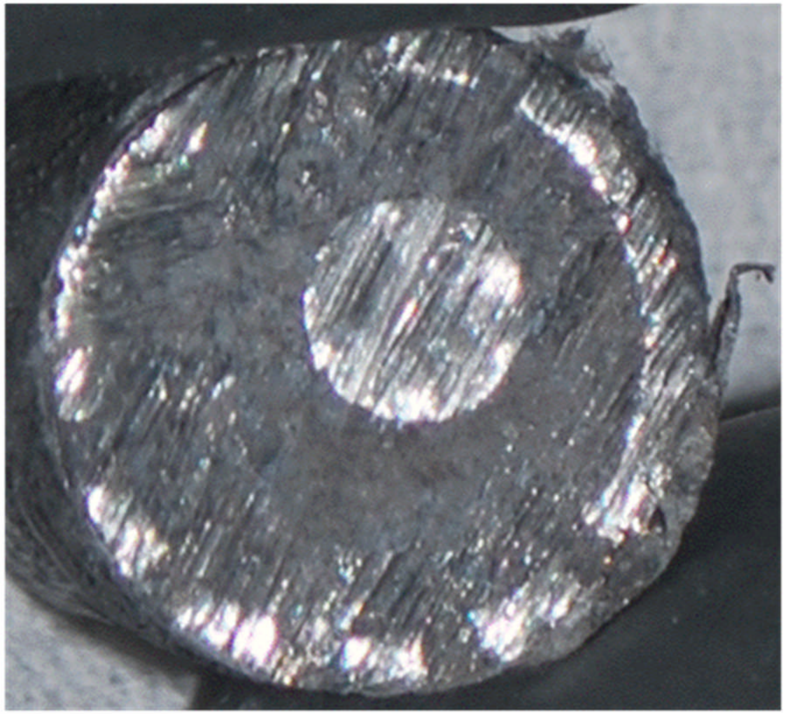
Electrolytic Reduction of MnO/ZrO_2 – Response Plot (Test 5)



Electrolytic Reduction – Post-Test Observations and Analysis



Basket section of reduced MnO particulate (test 4)



- Basket section of reduced MnO-ZrO_2 particulate (test 5)
- 73% of Mn and 9.6% of Zr observed in metal phase via ethyl-acetate / bromine dissolution method

Summary and Conclusions

Solid – Liquid Contacting Tests

- ZrO_2 addition to LiCl-Li_2O at 650 ° C exhibited rapid Li_2O depletion and Li_2ZrO_3 formation, consistent with the following thermodynamically favored mechanism.
  - *$ZrO_2 + Li_2O \rightarrow Li_2ZrO_3$* *($\Delta G_{f,\ 650C}$ = -66 kJ)*
- Zr metal (wire and particulate) additions to LiCl-Li_2O at 650 ° C exhibited Li_2O depletion along with Li_2ZrO_3 and Li metal formation, consistent with the following thermodynamically favored mechanism.
  - *$Zr + 3\ Li_2O \rightarrow Li_2ZrO_3 + 4\ Li$* *($\Delta G_{f,\ 650C}$ = -38 kJ)*

Electrolytic Reduction Tests

- Electrolytic reduction of MnO particulate and blended MnO – ZrO_2 particulate showed substantial reduction of Mn, but little reduction of Zr.

Conclusion

- LiCl-Li_2O-based electrolytic reduction is ineffective at substantially reducing zirconium oxide due to the thermodynamically favored lithium zirconate formation.

U.S. DEPARTMENT OF ENERGY

Nuclear Energy

Implications

- While electrolytic reduction of oxidized EBR-II U-10Zr fuel in LiCl-Li_2O at 650 ° C may be effective at uranium reduction to support subsequent electrorefining, the presence of lithium zirconate could interfere with the electrorefining of uranium.
- Similarly, the introduction of Zircaloy cladding from light water reactor fuel to an integrated electrolytic reduction and electrorefining process could be problematic.